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Hydrothermal quartz-baryte veins containing Pb-Cu-Sb-(Bi) mineralization at Brusno-Brzáčka occurrence (Veporic Unit, Central Slovakia) and their supergene alteration

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Abstract: The Brusno-Brzáčka occurrence (N 48.7698772°; E 19.4128150°) is located near the Brusno village (Slovenské Rudohorie Mts. Veporic Unit). Historically, the mineralization was explored by small-scale mining works located at the contact between the siliciclastic rocks of the Upper Permian and the Lower Triassic age. Paleo-Alpine metamorphic-hydrothermal mineralization is represented by quartz, baryte, or quartz-baryte veins, containing weak ore mineralization. Its succession is as follows: coarse-grained quartz I, pyrite (mineralization period I); baryte (II); tetrahedrite-(Zn), chalcopyrite (III); galena (IV) and quartz II (V). Supergene alteration produced initially covellite and spionkopite in the cementation zone. The oldest minerals in the oxidation zone are goethite, pyromorphite and mimetite. They were succeeded by the crystallization of Ba-rich anglesite, which partly overlaps in time with the precipitation of slightly younger anglesite. The formation of baryte partly overlaps with the deposition of anglesite, but in most cases, it is clearly younger. Bismutite is the youngest supergene mineral. A solid solution of anglesite–baryte with a Ba content from 0.29 *apfu* up to 0.51 *apfu* (i.e., Ba-rich anglesite) was identified at the studied site. This mineral phase covers the field of immiscibility of the natural solid solution $\text{PbSO}_4 - \text{BaSO}_4$, but the Ba/Pb ratio practically does not enter the baryte field (Pb-rich baryte).

Keywords: sulphide mineralization, quartz-baryte vein, supergene alteration, baryte-anglesite solid solution, Veporic Unit, Slovenské Rudohorie Mts., Western Carpathians

1 Introduction

There are several small historic deposits and mineralogical occurrences of Fe, Cu, Ag, and Sb ores in the northern part of the Veporic Superunit of the Western Carpathians (Plašienka et al., 1997). The most important ones are located around the villages of Špania Dolina, Staré Hory, Poniky, Ľubietová, and Čierny Balog. Less known occurrences of Cu, Fe, Pb, Zn, Ag, As, and Au mineralization were also found near the villages of Šumiac, Bacúch, Beňuš, Pohronská Polhora, Polomka, or Harmanec (Slavkay & Petro, 1993; Slavkay et al., 2004).

One of these occurrences is represented by the hydrothermal quartz-baryte veins with poor Pb-Cu-Sb-(Bi) mineralization at the Brusno-Brzáčka locality, south of Brusno village. The data on this occurrence are very austere (Hvožd'ara, 1971, 1980). The presented contribution expands basic knowledge about the nature of primary mineralization at this locality and is also dedicated to the mineralogical characteristics of its supergene transformation.

2 Geological setting of a wider area

The Western Carpathians Mts. located in Central Europe are a part of the Alpine-Himalayan Mountain range. Today's geological structure of the Western Carpathians is the result of complex geotectonic events during the Variscan and Alpine orogeny. The Western Carpathians are divided into two basic units, from the point of view of rock filling, the age of the tectonic individualization of the units and their mutual relations: externides and internides. The internides are built by a system of the Fatric, Hronic, and Silicic nappes, and the thick-skinned nappes (main tectonic superunits with crystalline complexes) – Tatric, Veporic, and Gemeric. Those are thrust onto each other in the general direction from the S to N (Tatric is the structurally lowest and northernmost unit), in a frame of the Alpine Orogeny style (Mahel' et al., 1967; Mazúr & Lukniš, 1980, 1986; Putiš, 1992; Plašienka et al., 1997; Plašienka, 1999; Hók et al., 2014, 2019; Kováč & Plašienka, 2003). The geological setting of the Veporic Unit is mainly formed by a crystalline basement of the Palaeozoic age and the autochthonous cover of the Upper Palaeozoic (Upper Permian) to Mesozoic (Lower Cretaceous) stratigraphic range (Siegel, 1982; Vozárová & Vozár, 1988; Hók et al., 2019; Slavkay et al., 2004; Antalík & Káčer, 2005).

The area of interest lies in the wider region of the Ľubietová zone – Veľký Bok cover sequence of the Veporic Unit (Zoubek, 1936, 1957) and particularly in the Upper Paleozoic rocks of a Northern Veporic cover (Vozárová, 1979). The Ľubietová zone consists of three, NE–SW oriented, segments differing in their lithology (Slavkay et al., 2004; Lexa et al., 2007). It is lithologically composed of various rocks: orthogneisses to migmatites with bodies of amphibolites, leucocratic granites, and paragneisses.

The sedimentary cover of the Northern Veporic crystalline basement is formed by Permian sequences of the Ľubietová Group (Slavkay et al., 2004). Vozárová (1979) recognised two lithostratigraphic units here – the lower Brusno and the upper Predajná formations. The rocks of both formations (originally continental coarse-grained clastic sediments of the "red-beds" type) were metamorphosed in the quartz-muscovite-chlorite subfacies of greenschist facies during the Alpine orogeny (Vozárová, 1979). The Brusno Formation (Lower Permian) is built up of weakly metamorphosed conglomerates, arkoses, cherts, and volcanic rocks. The upper part is

characterised by the presence of the volcanogenic horizon of Harnobis (rhyodacite and andesite tuff to ignimbrite, epiclastics and lava flows; Slavkay et al., 2004). The Predajná Formation (Upper Permian) is formed by successions of varied sandstones, polymict conglomerates and sandy shales (Vozárová, 1979; Slavkay et al., 2004). The Permian age of the sediments is evidenced by the palynomorph community (Planderová & Vozárová, 1982) and SHRIMP dating of magmatic zircons from Harnobis volcanics, which yielded ages of 273 ± 6 and 279 ± 4 Ma (Vozárová et al., 2016).

3 Localisation, geology and mineralogy

The studied Brusno-Brzáčka occurrence is located in the western part of the Slovenské Rudohorie Mts., in the Veporské vrchy Mts. (central Slovakia). The geological settings of the north-western part of the Slovenské Rudohorie Mts. were described by Polák et al. (2003^{a,b}).

The Brusno-Brzáčka occurrence is located about 3.6 km SSE of Brusno village, 4.5 km NE of Ľubietová village, approximately 750 m NW of the elevation point of Brzáčka (1005 m a. s. l.), at an altitude of about 780 m a. s. l. The geographical coordinates of the centre of occurrence (the adit under the forest road) are N 48.7698772°; E 19.4128150°.

In the past, perhaps in the 19th century, mineralization was explored by small-scale mining works (an adit, an exploration trench and several shafts were realised here). The gallery directs to the SSE (azimuth 160°). In addition, 9 shafts above the gallery and one short exploration trench in the direction of the SE (azimuth 132°) can be still found here.

The mining works are located at the contact between the Upper Permian rocks (Ľubietová Group) and the Lower Triassic rocks of the Veľký Bok cover sequence (Hvožd'ara, 1971, 1980; Koděra et al., 1986; Fig. 1). The Permian succession is represented by metaconglomerates, metasandstones, sandy shales, metarhyolites – metadacites and their volcanoclastics. The Lower Triassic formation is built by quartz sandstones, quartzites, conglomerates, sporadically shales and siltstones. In the vicinity of the adit, the rocks are relatively intensively tectonised and altered to fine-grained mylonites with newly formed white mica. Blocks of secretion quartz (size approximately 1×1 m) without ore mineralization are also found. The nature of primary mineralization can be assessed only based on material from the adit dump and forest road cuts. The heaps of the exploration shafts are devoid of ore material (except for rare pyrite in the quartz gangue).

The mineralogy of the occurrence was studied in the past by Hvožd'ara (1971, 1980), who found here primary baryte, quartz, pyrite, chalcopyrite, galena, and secondary goethite. In addition to these minerals, the results of the new revision of the site showed the presence of hematite and minerals of the tetrahedrite series (primary minerals). Supergene weathering products are represented by baryte, anglesite, bismutite, pyromorphite, mimetite, covellite, and spionkopite.

4 Methods

The ore samples for the mineralogical research were taken from the old adit dump and forest road cuts. The position of the individual mine works (adit, exploration trench and shafts) was targeted with a tourist GPS device with an accuracy of ± 5 m.

Microscopic properties of mineral phases were observed in both transmitted and reflected light (thin sections) using a Nikon ECLIPSE LV 100 POL polarizing microscope (Matej Bel University, Banská Bystrica).

The chemical composition of minerals was quantitatively studied using an electron microanalyzer Jeol-JXA-8530F (Institute of Earth Sciences SAS, Banská Bystrica) and Cameca SX-100 (National Museum, Prague, Czech Republic). In addition to point wavelength-dispersive microanalyses (WDS), the microanalyzer was also used for photo-documentation in backscattered electrons (BSE) and non-standardised energy-dispersive analyses (EDS). The WDS microanalyses were performed under the following conditions: acceleration voltage 20 and 25 kV, measurement current 15 and 20 nA and electron beam diameter 2–5 μm (sulphides) and 15 kV, measurement current 15 nA and 10 nA and electron beam diameter 1–10 μm (supergene minerals). The electron microanalyzer (EMP) was calibrated using natural and synthetic standards (Supplementary Table S1). The tables presented in the following text do not include elements whose content values were below the detection limit for individual elements (0.03–0.2 wt. %). The PAP (Pouchou & Pichoir, 1985) and ZAF corrections were used.

5 Primary (hydrothermal) minerals

The dominant filling of hydrothermal veins is monomineral quartz or baryte, but also quartz and baryte. Sulphide minerals are disseminated or rarely form nests (size to the first cm) in the gangue. The main sulphide minerals are pyrite and rarely galena, accompanied by chalcopyrite and tetrahedrite-(Zn). However, the ore mineralization is poor and the occurrence has only the character of an ore indication.

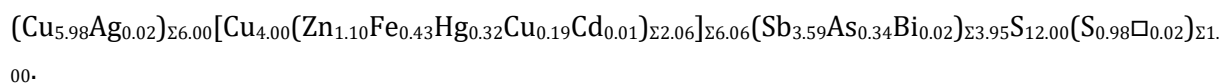
Pyrite is relatively abundant in small amounts. Its accumulations up to 2 cm in size were rarely found in the quartz gangue. Crushed anhedral pyrite grains and fine-grained clusters (up to 0.1 mm) are enclosed in tetrahedrite-(Zn), goethite, and anglesite (Fig. 2a,b). More rarely, they are surrounded by fine-grained white mica. The chemical composition of pyrite (1 WDS analysis) shows slightly increased contents of Cu (0.01 *apfu*).

Chalcopyrite forms local nests (up to 3 cm in size), especially in quartz gangue. The microscopic description practically coincides with pyrite, but chalcopyrite is not cataclased. It is younger than pyrite. Non-standardised EDS analyses did not show the presence of other elements.

Galena forms 3–4 mm large aggregates in quartz. Under the microscope, its considerable supergene transformation is evident. It is characterised by a system of cleavage cracks in three directions, accompanied by triangular pits. Galena tends to be surrounded by anglesite, which also replaces it along cracks. There are also small nests of covellite and spionkopite in anglesite. Sometimes anglesite forms complete pseudomorphs after galena, preserving the cubic shape of the original mineral (Fig. 2c,d). The chemical composition of galena is quite interesting (considering mainly the “pure” composition of other galenas in the Veporic Unit), but without

significant variations in the content of the elements (Tab. 1). In addition, to lead, Bi (average 0.02 *apfu*) and Ag (average 0.01 *apfu*) are present in the cationic position. Copper is less significant (up to 0.02 *apfu*). Besides to sulphur, a small amount of Se (up to 0.01 *apfu*) is present in the anionic position. The average empirical formula of galena from the Brzačka occurrence (7 WDS analyses) can be expressed as $(\text{Pb}_{0.97}\text{Bi}_{0.02}\text{Ag}_{0.01})_{\Sigma 1.00}\text{S}_{0.99}$.

Tetrahedrite-(Zn) is a rare mineral at the studied site. It forms irregular thin veinlets about 2–3 mm long, or individual grains up to 0.15 mm in size in baryte or quartz. It encloses crushed pyrite grains (Fig. 2b). The cracks in the tetrahedrite are filled with anglesite (which indicates an original filling with galena). In the BSE image, an indistinct zonality was detected, where lighter domains (more Zn and Sb) seem to be enclosed in a darker phase (Fig. 3). Chemical composition of tetrahedrite is given in Table 2. In the crystallochemical formula of the studied tetrahedrite, A position (*sensu* Biagioni et al., 2020) is almost entirely occupied by Cu (≈ 5.98 *apfu*), the silver content of the tetrahedrite is very low (up to 0.07 *apfu* Ag). In the B position, the dominant element is Zn (0.94–1.27 *apfu*), while the Fe and Hg contents were found in the range of 0.28–0.54 *apfu* and 0.19–0.50 *apfu*. From the relationships of the main elements occupying the B position, two substitution trends are evident in the studied tetrahedrite (Fig. 4). Less represented is the negative substitution $\text{Fe} \rightarrow \text{Zn}$, near relatively the same Hg content. The negative substitution $\text{Fe} + \text{Hg} \rightarrow \text{Zn}$ was detected to a greater extent. Position D is also characterised by a very small range of substitutions. The dominant element is Sb (average 3.59 *apfu*) and less represented is As (average 0.34 *apfu*). Locally, a slightly increased Bi content was detected (max. 0.07 *apfu*). The average chemical composition of tetrahedrite-(Zn) from the Brusno-Brzáčka occurrence (26 WDS analyses) can be expressed by the following crystal chemical formula:



Quartz is an abundant vein mineral in the locality. Its two generations were identified microscopically. The basic vein mineral is coarse-grained quartz I (grain size up to 0.5 cm) with manifestations of dynamometamorphism (cataclasis, undulosity, deformation lamellae, migration of grain edges). Quartz II forms veinlets up to 0.5 mm thick, crossing quartz I and accumulations of ore minerals (Fig. 5a). It is not undulose. Accumulations of fine-grained white mica were locally detected in both generations of quartz.

Baryte sometimes forms a substantial (or even the only) part of the gangue. Two of its generations (types, respectively) were observed. Baryte I is coarse-grained (grain size up to 3–4 mm) and shows signs of dynamometamorphism – mainly deformation lamellae (unlike quartz, baryte behaves plastically during deformation, so there are no signs of cataclasis). Dynamic recrystallization is manifested by the formation of newly formed baryte II, which forms veins along the grain boundaries of baryte I, composed of more or less isometric grains reaching around 0.1–0.3 mm in size (Fig. 5b). Chemical composition of the hydrothermal baryte is relatively monotonous (Tab. 3). Slightly elevated concentrations of Sr (0.05–0.09 *apfu*) are stably present. Locally there are other minor ones: Cu up to 0.03 *apfu*, Zn up to 0.01 and Na up to 0.02 *apfu*. Pb concentrations are below the minimum detection limit, but local values of 0.001–0.002 *apfu* were found. However, the increased content of these elements (mainly Cu) can also come from contamination from other mineral phases during analysis (contamination from “baryte footwall”

during point WDS analysis). The average chemical composition of hydrothermal baryte from the Brusno-Brzčka occurrence (12 WDS analyses) expresses the following empirical formula: $(\text{Ba}_{0.93}\text{Sr}_{0.06}\text{Cu}_{0.01}\text{Na}_{0.01})_{\Sigma 1.01}(\text{SO}_4)_{0.99}$.

6 Characteristics of the supergene minerals

The oxidation zone of the Brusno-Brzčka occurrence is poorly developed (appropriate to the weak development of primary mineralization), although the detected spectrum of minerals is relatively diverse. Secondary minerals appear in the form of veins, clusters and irregular grains mainly in quartz. Locally, they form complete pseudomorphs after aggregates of primary ore minerals. Supergene weathering products are represented by baryte, anglesite, bismutite, pyromorphite, mimetite, covellite, and spionkopite.

Baryte of supergene origin is relatively rare at the site. It forms irregular veinlets crossing anglesite and quartz (Fig. 6a). The chemical composition of baryte was studied only informatively (1 WDS analysis; Tab. 3). Contrary to the hydrothermal baryte, supergene one is characterised by a low content of other elements: Pb 0.003 *apfu* and Sr up to 0.002. The empirical formula of baryte approaches the ideal BaSO_4 .

Anglesite is a relatively abundant supergene mineral in the studied occurrence. It partially or completely replaces galena, the shape of its irregular aggregates copies the shape of the original galena aggregates (Fig. 6b,c). It is most often associated with its variety of Ba-rich anglesite. The studied anglesite (Tab. 4) contains minor other elements, Bi (up to 0.12 *apfu*), Cu (up to 0.08 *apfu*) and Ba (up to 0.07 *apfu*). In addition to dominant sulphur, Se enters the anion position in a minor amount (up to 0.03 *apfu*). The empirical anglesite formula from Brusno-Brzčka (5 WDS microanalyses) can be expressed as follows: $(\text{Pb}_{0.92}\text{Ba}_{0.05}\text{Bi}_{0.04}\text{Cu}_{0.02}\text{Fe}_{0.01})_{\Sigma 1.03}(\text{SO}_4)_{0.99}$.

The mineralogically noteworthy phase of the studied site is the **Ba-rich anglesite**. It is often intergrown with slightly younger anglesite (without Ba), forming irregular aggregates (Fig. 6c). In the chemical composition of the transitional mineral phase of the baryte-anglesite series (Tab. 5), we detected minor contents of Zn (max. 0.01 *apfu*), Fe (up to 0.02 *apfu*), Sr (up to 0.02 *apfu*), Cu (up to 0.03 *apfu*) and locally increased Bi (up to 0.13 *apfu*). Ba-rich anglesite is characterised by significant Ba \rightarrow Pb substitution (0.12–0.51 *apfu* Ba; 0.50–0.88 *apfu* Pb). Selenium (up to 0.06 *apfu*) occasionally enters the anionic X position. The average chemical composition of the studied Ba-rich anglesite (16 points WDS analyses) expresses an empirical formula $(\text{Pb}_{0.66}\text{Ba}_{0.34})_{\Sigma 1.00}(\text{SO}_4)$. Based on the nomenclature rule of 50%, the studied mineral phase lies practically only in the anglesite field (Fig. 7).

The accessory mineral of the Brusno-Brzčka locality is **bismutite**, $\text{Bi}_2(\text{CO}_3)\text{O}_2$, which forms veinlets in anglesite (Fig. 6a, 8). Microprobe analyses of bismutite revealed significant enrichment in Pb (up to 0.24 *apfu*) and Sb (up to 0.08 *apfu*), to a lesser extent Fe (up to 0.04 *apfu*) and Cu (up to 0.01 *apfu*), at the expense of Bi_2O_3 content (max. 1.58 *apfu* Bi). A slightly increased content of S was detected in the anionic position (up to 0.05 *apfu*; Tab. 6). The average empirical formula of the studied mineral phase (2 WDS analyses) is: $(\text{Bi}_{1.57}\text{Pb}_{0.23}\text{Sb}_{0.08}\text{Fe}_{0.04}\text{Cu}_{0.01})_{\Sigma 1.93}[(\text{CO}_3)_{0.90}(\text{SO}_4)_{0.05}(\text{SeO}_4)_{0.01}(\text{PO}_4)_{0.01}]_{\Sigma 0.97}\text{O}_2$.

Pyromorphite is locally found in association with younger anglesite (Fig. 9a). The studied pyromorphite differs from the ideal chemical composition, $\text{Pb}_5(\text{PO}_4)_3\text{Cl}$, by the presence of increased Fe contents (0.09–0.15 *apfu*) and minor contents of Sr, Sb, and Bi (up to 0.06 *apfu*; for each element separately). Interesting are the significant Cu contents varying in the range of 0.14 to 0.28 *apfu*. In addition to the majority of P (1.88–2.82 *apfu*), S (0.02–0.22 *apfu*) and As (up to 0.68 *apfu*) are also present at the anion position. The significant As \rightarrow P substitution was also detected (0.52–1.22 *apfu* As; Fig. 10). Chlorine dominates in all analyses of pyromorphite, its amount ranges from 0.80 to 0.92 *apfu*. The chemical composition of pyromorphite is shown in Table 7. The average empirical formula of pyromorphite (7 WDS microanalyses) from Brusno-Brzčka occurrence is $(\text{Pb}_{4.47}\text{Ca}_{0.19}\text{Cu}_{0.16}\text{Fe}_{0.10}\text{Sb}_{0.02}\text{Bi}_{0.02}\text{Sr}_{0.02}\text{Zn}_{0.02}\text{Ba}_{0.01})_{\Sigma 5.00}[(\text{PO}_4)_{2.24}(\text{AsO}_4)_{0.42}(\text{CO}_2)_{0.25}(\text{SO}_4)_{0.09}]_{\Sigma 3.00}(\text{Cl}_{0.90}\text{OH}_{0.10})_{\Sigma 1.00}$.

Mimetite was most often found in association with baryte and anglesite (Fig. 9b). Representative analyses of mimetite are given in Table 8. In addition to dominant Pb, Bi (0.02–0.05 *apfu*), Sr (up to 0.07 *apfu*) and Sb (0.01–0.04 *apfu*) enter the cationic position. Low contents of Cu (up to 0.01 *apfu*), Ba (up to 0.04 *apfu*) and Fe (up to 0.04 *apfu*) were found locally. The anionic position is dominantly occupied by As (2.56–2.64 *apfu*), and the content of S is significantly increased (0.18–0.20 *apfu*). In contrast to pyromorphite, isomorphic substitution $\text{P} \rightarrow \text{As}$ is practically absent in mimetite (0.04–0.07 *apfu* P; Fig. 10). The Cl content ranges from 0.95 to 0.99 *apfu*. The average crystal chemical formula of mimetite (10 WDS analyses) can be expressed as $(\text{Pb}_{4.89}\text{Bi}_{0.03}\text{Sr}_{0.03}\text{Fe}_{0.02}\text{Sb}_{0.01}\text{Cu}_{0.01}\text{Ba}_{0.01})_{\Sigma 5.00}[(\text{AsO}_4)_{2.61}(\text{SO}_4)_{0.19}(\text{PO}_4)_{0.05}(\text{CO}_2)_{0.15}]_{\Sigma 3.00}(\text{Cl}_{0.97}\text{OH}_{0.03})_{\Sigma 1.00}$.

Goethite is a relatively common mineral phase in small amounts. It most often forms dark brown and rusty thin coatings on the surface of mineralised samples. Unspecified Fe oxides form yellowish-brown earthy masses in cavities of quartz (pseudomorphoses after original pyrite aggregates).

7 Mineral phases of Cu-S system

Minerals of the Cu-S system form fine coatings and fissure fillings of various shades of blue. They replace galena along the cracks and edges of its aggregates (Fig. 2d) in association with anglesite or Ba-rich anglesite. A relatively abundant mineral at the Brusno-Brzčka locality is covellite, with a ratio of cations/anions $\sim 0.99/1$ (1/1 in ideal covellite). In its chemical composition (Tab. 9), enrichment of Ag (up to 0.05 *apfu*) and a small content of other elements (Zn, Se – less than 0.01 *apfu* in total) was detected. The average empirical formula of covellite (13 WDS analyses) can be expressed as $(\text{Cu}_{3.94}\text{Ag}_{0.06})_{\Sigma 4}\text{Cu}_{2.06}(\text{S}_{1.99}\text{Se}_{0.01})_{\Sigma 2}\text{S}_{4.07}$. The cation/anion ratio in the mineral phase close to spionkopite ranges from 1.28–1.30/1 (1.4/1 in ideal spionkopite). The studied mineral phase differs from the ideal chemical composition by the presence of additional components Ag (up to 0.47 *apfu*), Bi (up to 0.04), and Zn (max. 0.01 *apfu*). From the average of two point WDS analyses (Tab. 9), the chemical composition of spionkopite from the Brusno-Brzčka site can be expressed as $(\text{Cu}_{14.56}\text{Ag}_{0.44})_{\Sigma 15.00}(\text{Cu}_{4.44}\text{Bi}_{0.04}\text{Zn}_{0.01})_{\Sigma 4.50}(\text{S}_{1.93}\text{Se}_{0.07})_{\Sigma 2.00}(\text{S})_{13.15}$. Both minerals formulae are expressed in an extended form (*sensu* Goble, 1985).

8 Discussion and conclusions

8.1 Evolution and genesis of primary (hydrothermal) mineralization

A consequence of the weak development of mineralization is the mutual isolation of individual aggregates of ore minerals or the mineral phases themselves, which does not allow relevant determination of their mutual microstructural relationships. Another reason is the poor terrain exposure – mineralised samples were taken at points and more or less randomly, without the possibility of studying mineralization directly in the outcrops or the adit. Nevertheless, it is possible to roughly determine its development based on the relationships of primary and supergene minerals, also based on correlation with succession schemes of more significant and better-studied ore deposits/occurrences in the Veporic or Gemeric units.

Within the **hydrothermal phase** of the development of mineralization, the oldest minerals are coarse-grained **quartz I** (main gangue mineral) and **pyrite** (*mineralization period I*). Afterwards, **baryte** was deposited (*mineralization period II*). In the *period III*, **tetrahedrite-(Zn)** and **chalcopyrite** were formed. Precipitation of **galena** took place already in *period IV*. Clusters of primary ore minerals (also complete pseudomorphs of supergene minerals after them) are cut by thin veinlets of **quartz II** (*period V*).

The character of hydrothermal mineralization at the studied site is similar to that at the nearby Ľubietová-Peklo occurrence in the Northern Veporic Unit (Ferenc et al., 2019), or the occurrences of siderite-sulphidic mineralization at Uderiná, Lovinobaňa and Cinobaňa in the Southern Veporic Unit (Ferenc et al., 2014). It can also be roughly compared with the evolution of siderite-sulphidic hydrothermal mineralization in the Spišsko-Gemerské Rudohorie in the Gemeric Unit (Cambel & Jarkovský, 1985; Hurai et al., 2008). In the case of the Brusno-Brzáčka occurrence, the carbonate period was not found. The reason thereof could be also the total conversion of carbonates to Fe oxides. The overall very weak development of mineralization should be emphasized again.

The geological position of the occurrence at a contact zone between Upper Permian and Lower Triassic sedimentary rocks (Slavkay et al., 2004) as well as the nature of the hydrothermal mineralization clearly indicate its Paleo-Alpine age. The ore minerals were probably formed during mild dynamometamorphism, which is evidenced by the transformation of clastic sediments into sericite phyllites, pressure lamellae, migration of mineral grain edges and newly formed grains in pre-existing quartz I and baryte. It is therefore a metamorphic-hydrothermal mineralization. Lexa et al. (2007) place this occurrence to the Paleo-Alpine, late orogenic metallogenetic stage of the Slovak part of the Carpathians development (90–70 Ma; Late Cretaceous). The temperature conditions of Alpine metamorphism in the Northern Veporic did not exceed 350 °C, while the maximum temperatures were reached in the period between about 80–70 Ma (e.g., Plašienka, 2018; Majzlan et al., 2022). It can therefore be assumed that the studied hydrothermal mineralization at the Brusno-Brzáčka occurrence was formed after the peak of metamorphism during cooling of the system, perhaps in the Late Cretaceous period.

8.2 Notes on the evolution of supergene zone

In contrast to the hydrothermal phase, the relationships among minerals formed in the **supergene phase** of mineralization are somewhat clearer. The Cu-S sulphides **covellite** and **spionkopite** formed in the first oxidation stage of preexisting sulphidic minerals. Oxidizing conditions began to prevail as the erosion cut progressed. Probably the oldest **oxidation zone** minerals are **goethite**, **pyromorphite**, and **mimetite**. They were followed by the crystallization of **Ba-rich anglesite**, which overlaps in time with the precipitation of slightly younger **anglesite**. The formation of **baryte** partly overlaps with the deposition of anglesite, but in most cases, it is clearly younger. Rare bismutite is probably the youngest oxidation mineral. A similar evolution of the supergene zone (sulphides → arsenates → sulphates → carbonates) was detected within the Cu-As-Pb-Zn mineralization at the Cap Garonne deposit in France (Poot et al., 2023). A more advanced stage of supergene alteration of galena (with practically the same association of supergene minerals), documented by the dissolution of cerussite and anglesite, is reported by Keim & Markl (2015). Direct replacement of galena by anglesite has been found in many cases, while the alteration of anglesite to other supergene phases (e.g., carbonates) is the result of a change in the chemical composition of supergene solutions accompanied by a decrease in the concentration of sulphate ions (Williams, 1990). Neglecting the extremely rare occurrence of bismutite, the absence of carbonates at the site therefore reflects a very low concentration of dissolved CO_3^{2-} ions in the supergene solutions. This is caused by the fact that the host rocks (Lower Triassic and Permian clastic sediments) have neither a carbonate matrix nor carbonate clasts.

The supergene zone at the Brusno-Brzázka occurrence is very weakly developed. Despite this, some mineral phases (bismutite, mimetite, pyromorphite), or interesting baryte-anglesite solid solution, which are still relatively rare for Slovakia, were found in the apparently weakly mineralised samples. Also noteworthy is the slightly increased bismuth content, the main carrier of which is galena (on average 0.015 *apfu* Bi), less Bi is present in tetrahedrite-(Zn) (0.017 *apfu* Bi on average). Due to the supergene alteration, mainly of galena, bismuth enters the secondary minerals, either as the major element (bismutite; ~ 1.57 *apfu* Bi), or as a minor element, e.g., in anglesite and Ba-rich anglesite (on average 0.040 *apfu* Bi), also in pyromorphite (~ 0.05 *apfu* Bi) and mimetite (~ 0.07 *apfu* Bi).

8.3 About *bario-anglesite* (Ba-rich anglesite)

Baryte-group minerals are defined by a general chemical formula AXO_4 , in which the A position is occupied by divalent Ba, Sr, or Pb ions and the X position is occupied by S^{6+} or Cr^{6+} ions. Baryte is the most common member of the baryte group, the other three are anglesite (PbSO_4), celestine (SrSO_4) and hashemite (BaCrO_4). Thus, the difference in chemical composition is represented only by their metal cations. Strontium and lead, with their similar valences and ionic radii, easily replace Ba. Barium and strontium replace each other very easily, therefore baryte and celestine form a complete series of solid solutions with intermediate phases like barium-celestine, “*celestobarite*”, or “*baritocelastine*”. Baryte also forms a partial solid solution series with anglesite, with an intermediate phase known as “*plumbobarite*” (Klein & Philpotts, 2013; Johnson et al.,

2017). In the past, Pb-rich baryte was also referred to as “*hokutolite*” or “*anglesobarite*”. Generally, it is a rare mineral phase, found in only a few occurrences in the world. It was first discovered in 1905 at the Peitou locality (Hokuto; Chang, 1961) Springs (Taiwan; mindat.org). In Japan, Pb-rich baryte was found at Tamagawa Hot Springs and Kawarge localities. In these sites, it crystallised from hyperacidic (pH <2), SO₄ - Cl geothermal waters, at a temperature of around 60 °C (Takano et al., 1969; Yoshiike, 2003). Such Pb-rich baryte is also a bearer of certain amounts of Ra, as well as U and Th, therefore it is possible to search for it in places of natural occurrence also based on increased radioactivity (Momoshima et al., 1997; Tomita et al., 2006; Chao et al., 2009). In addition, microcrystals of the baryte-anglesite solid solution were found on heaps after mining activities, e.g. the Sandsloot mine site in South Africa (mindat.org/min-9160.html; Courtin-Nomade et al., 2008), Cínovec in Czech Republic (Pauliš et al., 1998) and in contaminated soils (Caboche et al., 2010).

In the literature, the completeness of the PbSO₄ – BaSO₄ solid solution is quite often discussed in terms of metastability, or the immiscibility of phases with a certain Pb/Ba ratio (Takano et al., 1969; Takiyama, 1967; Boström et al., 1967). Based on analytical data (Fig. 7 and the references therein), it is known that the natural Pb-rich baryte contains max. ~ 47 mol. % PbSO₄. On the contrary, it was possible to synthesize a complete PbSO₄ – BaSO₄ solid solution under laboratory conditions (Wang et al., 2002; Lee et al., 2005).

At the Brusno-Brzáčka occurrence, we identified the baryte-anglesite solid solution (Ba-rich anglesite) with a Ba content from 0.002 *apfu* up to 0.51 *apfu* Ba. This mineral phase covers the field of immiscibility of the natural PbSO₄-BaSO₄ solid solution (Fig. 7), but the Ba/Pb ratio practically does not enter the baryte field. The Ba-rich anglesite was formed here under supergene conditions, from cold, probably slightly to moderately acidic near-surface solutions. In the locality, the average annual air temperature is 4–6 °C, and the average annual temperature of the soil surface is 7–8 °C (Atlas of the landscape of Slovak Republic, online). Most amounts of Pb-rich baryte are formed mainly from hyperacidic and tempered solutions (60 °C), much less under supergene conditions (Takano et al., 1969; Yoshiike, 2003; Courtin-Nomade et al., 2008; Caboche et al., 2010). This fact indicates, that natural members of solid solution with Ba/(Ba+Pb) ratio in the range of 0.002–0.50 (corresponding to Ba-rich anglesite) can be preferentially formed from cold solutions, whereas members with Ba/(Ba+Pb) ranging 0.53–0.99 (i.e., corresponding to Pb-rich baryte) preferentially precipitate at higher temperatures.

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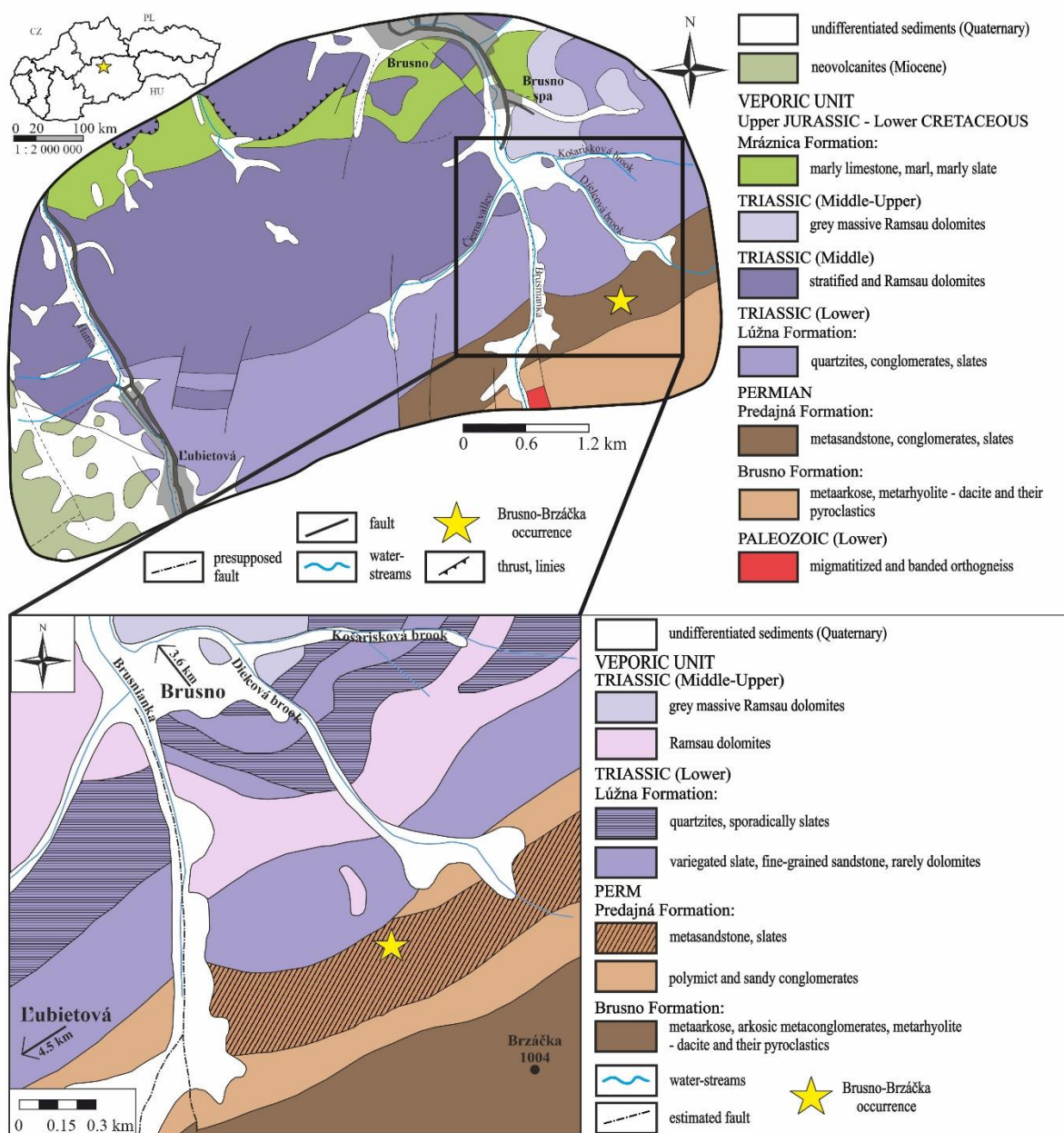
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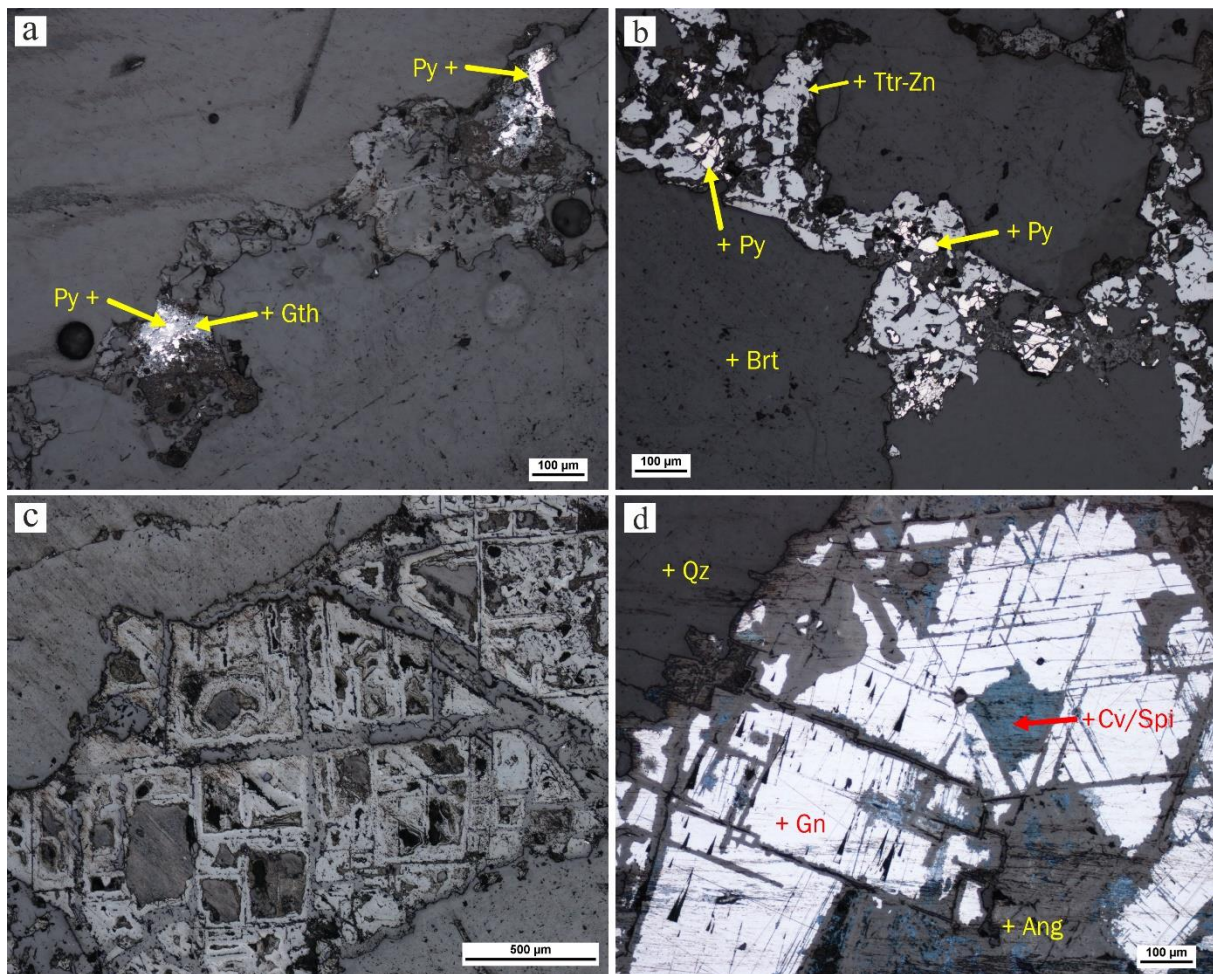


Fig. 2: **a)** Irregular pyrite (Py) nests partially replaced by goethite (Gth) in a veinlet of unspecified supergene minerals in quartz. **b)** Tetrahedrite-(Zn) (Ttr-Zn) forms a veinlet in baryte (Brt) and encloses allotriomorphic, cataclased pyrite grains (Py). **c)** Complete pseudomorphosis of anglesite (lighter, cubic shapes) after galena aggregate in quartz (darker). **d)** Galena (Gn) is pervasively and along cleavage planes replaced by anglesite (Ang). Covellite and spinkopite aggregates (Cv/Spi, blue) are present in anglesite. All pictures – reflected light, PPL. Photo: Š. Ferenc.

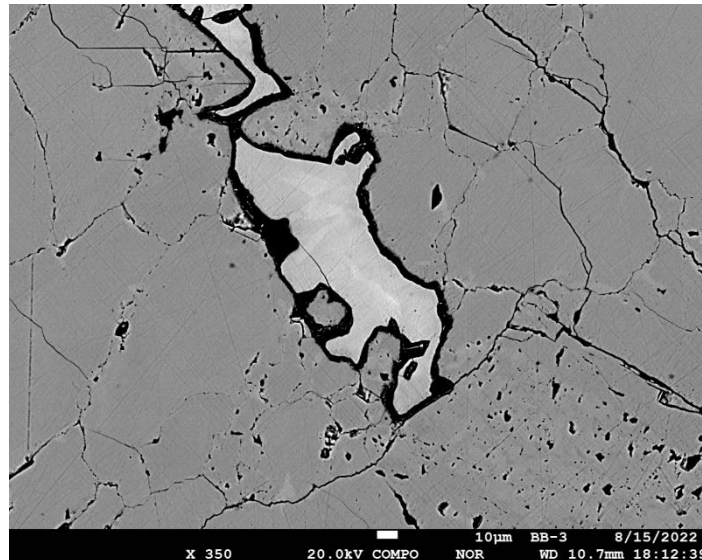


Fig. 3: Irregular veinlet of tetrahedrite-(Zn) (light grey) in baryte (darker). Tetrahedrite is zonal - lighter zones contain more Zn and Sb than darker ones. BSE image. Photo: T. Mikuš.

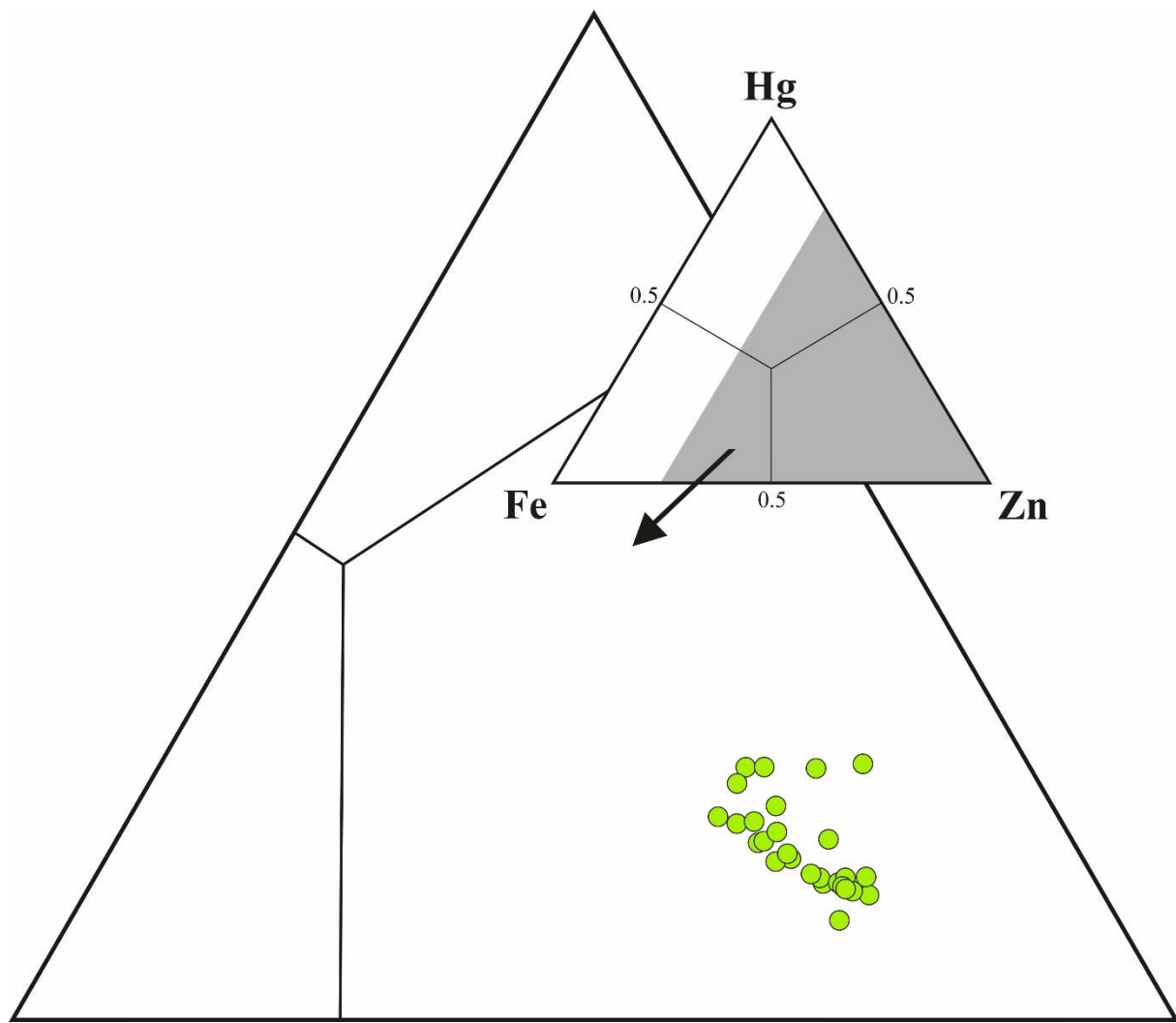


Fig. 4: Composition of the studied tetrahedrite-(Zn) from the Brusno-Brzacka (*apfu*) in the Fe-Zn-Hg ternary diagram.

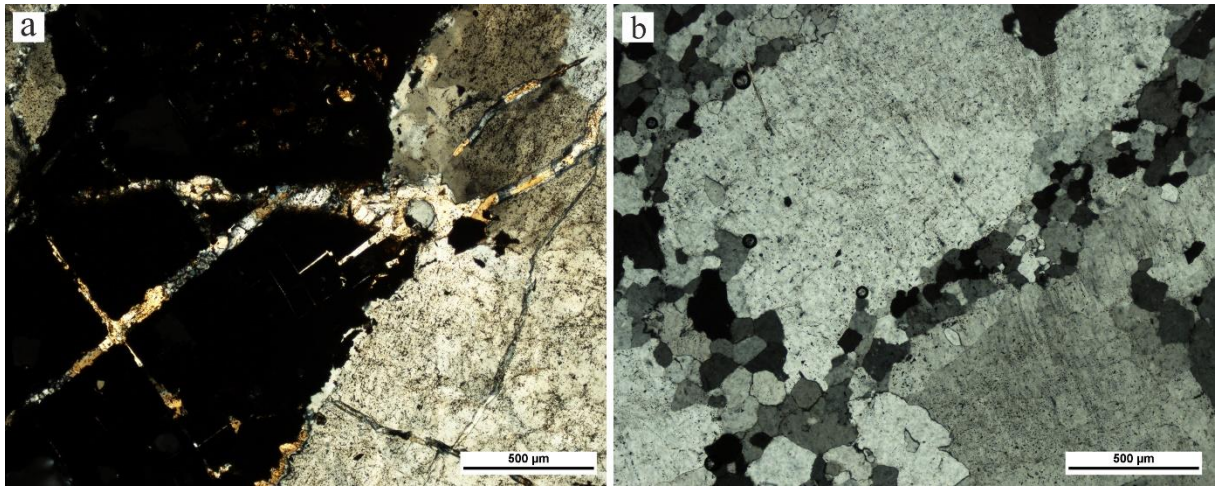


Fig. 5: **a)** Aggregate of ore minerals (black) in coarsely crystalline quartz I. Ore minerals as well as older quartz are intersected by younger quartz II. **b)** Hydrothermal baryte with manifestations of dynamometamorphism (formation of newly formed baryte grains, deformation lamellae). Both images – transmitted light, XPL. Photo: Š. Ferenc.

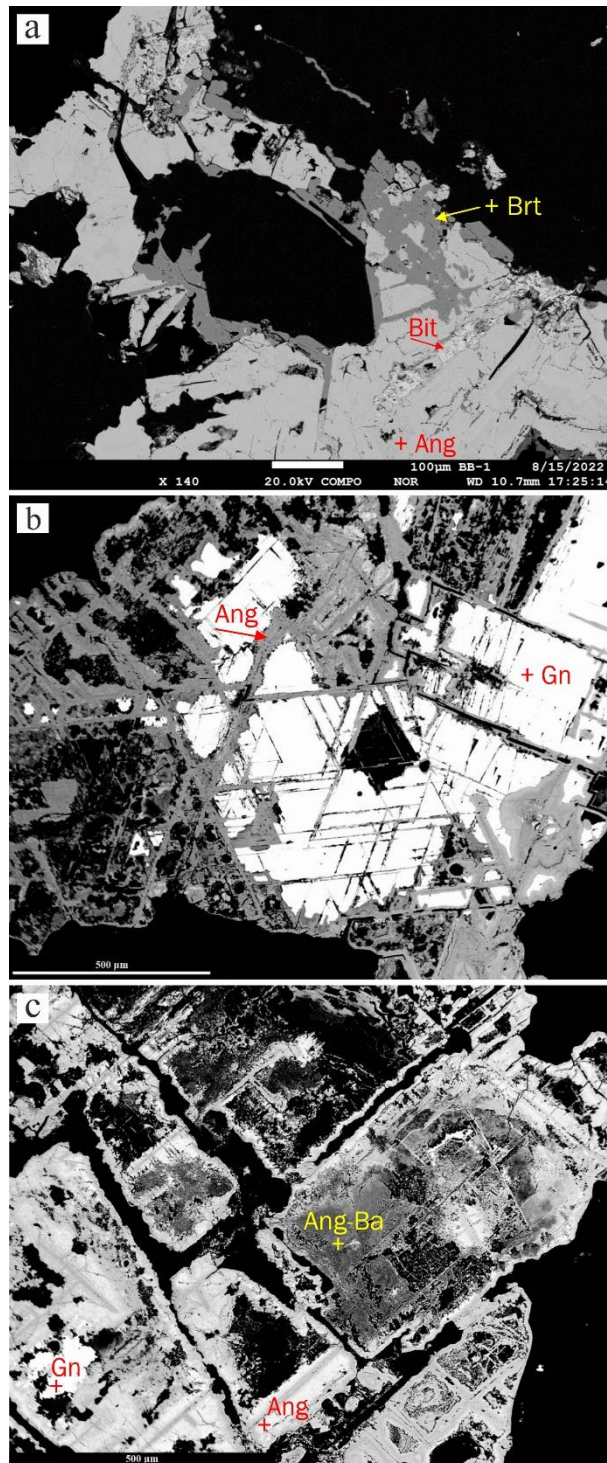


Fig 6: **a)** Bismutite veinlet (Bit) in anglesite (Ang). Baryte (Brt) rims and cut the anglesite aggregate. **b)** Galena (Gn) replaced by anglesite (Ang) along cleavage. **c)** Anglesite (Ang) and Ba-rich anglesite (Ang-Ba) pseudomorphs after cubic galena. BSE pictures. Photo: T. Mikuš.

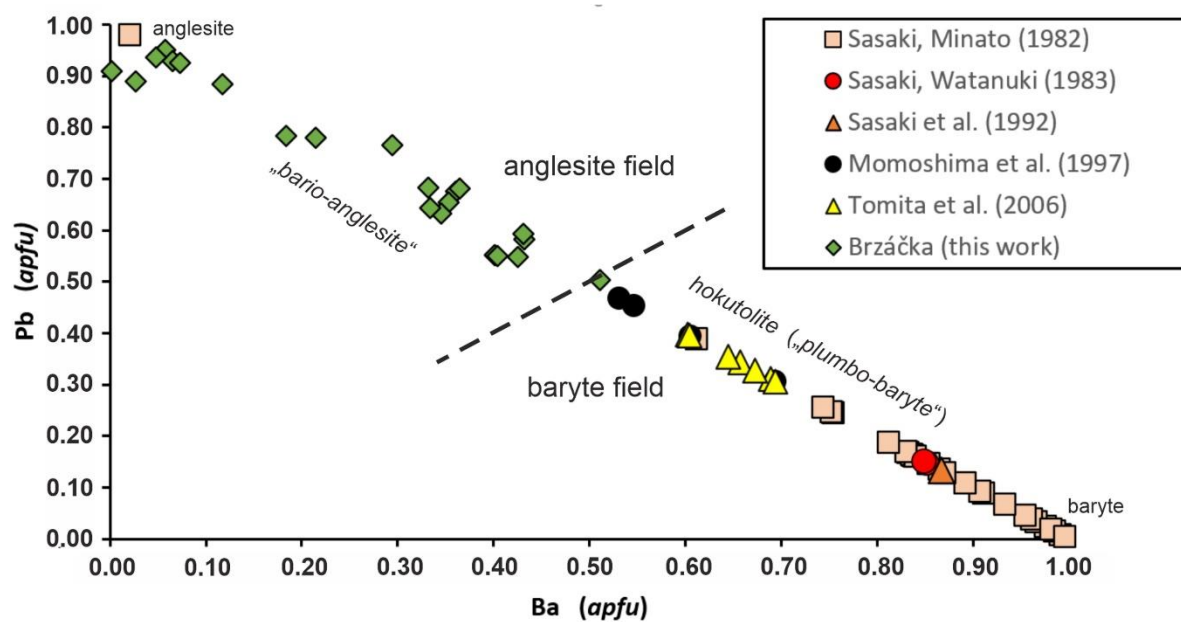


Fig. 7: Ba vs. Pb contents in Ba-rich anglesite from the Brusno-Brzáčka compared to Pb-rich baryte (“hokutolite”).

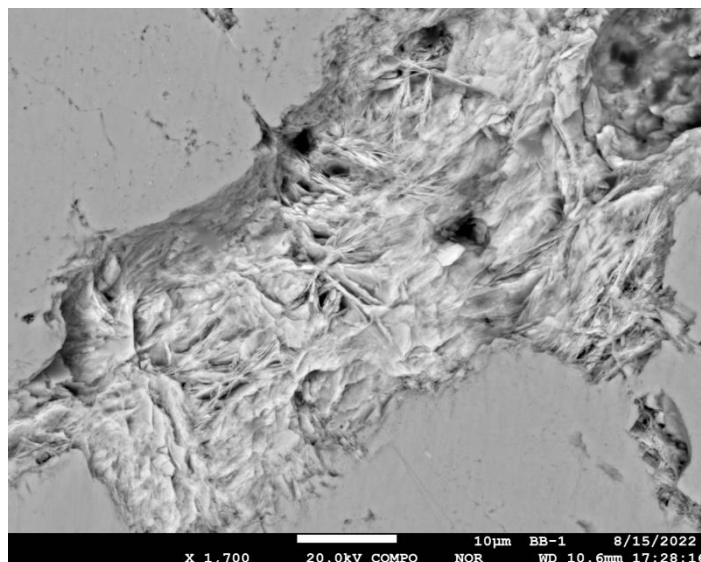


Fig. 8: Detailed view of a bismutite aggregate hosted by anglesite (dark gray, compact), BSE image. Photo: T. Mikuš.

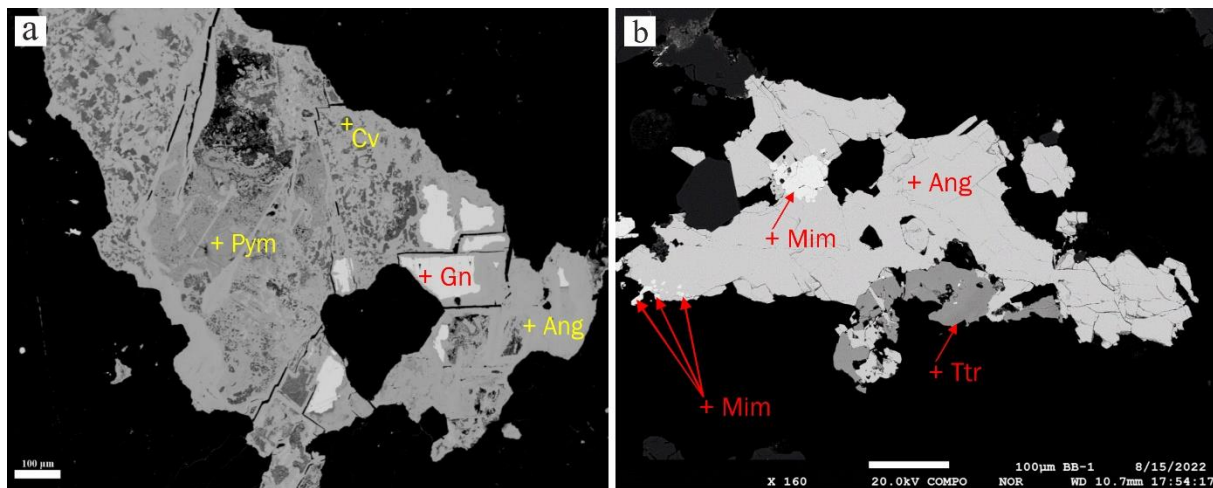


Fig. 9: **a)** Pyromorphite aggregate (Pym) rimmed and cut by anglesite (Ang). Covellite (Cv) forms fine-grained aggregates and galena (Gn) forms relicts in anglesite. **b)** Mimetite (Mim) forms irregular grains in anglesite (Ang). The replacing of tetrahedrite (Ttr) by anglesite, indicates the original replacing of tetrahedrite by galena. BSE images. Photo: T. Mikuš.

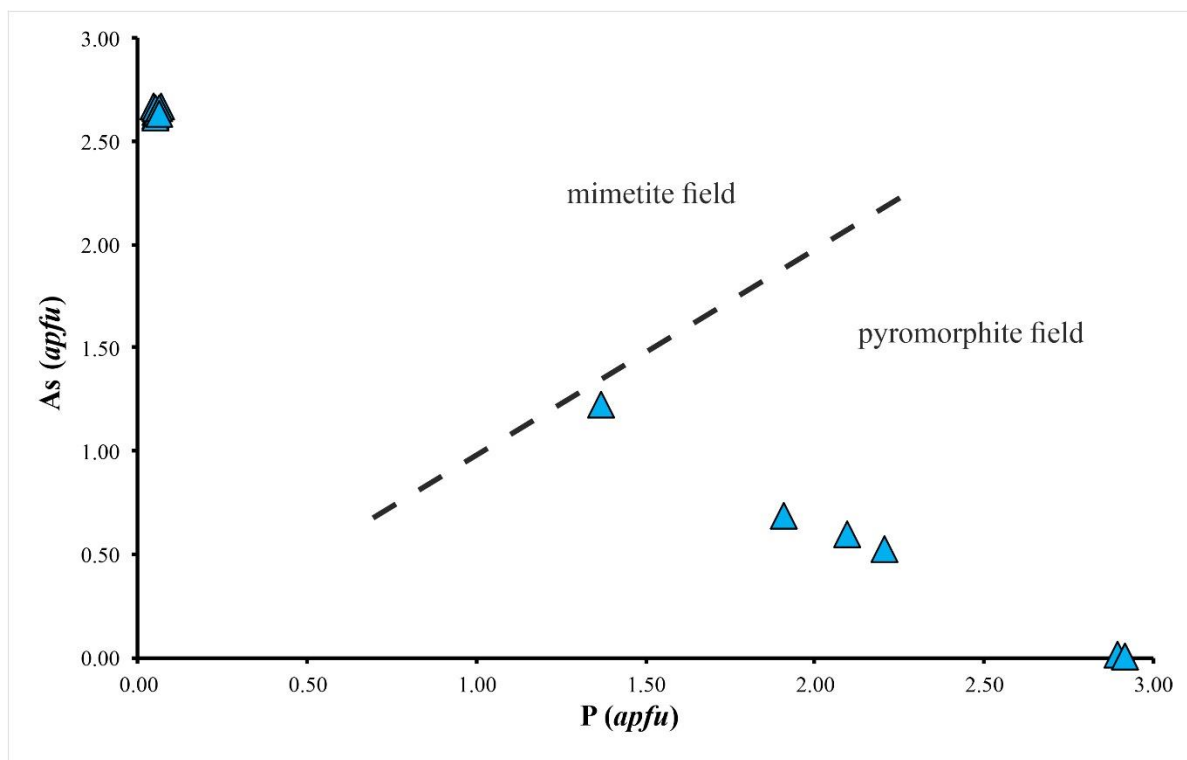


Fig. 10: Variations of the anionic position of pyromorphite and mimetite in the diagram P vs. As.